



Synthesis of a catalytic support from natural cellulose fibers, and its performance in a CO₂ reforming of CH₄

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ABSTRACT

Porous carbon was synthesized from natural cellulose fibers and its performance as a catalytic support was investigated for a CO₂ reforming of CH₄. Ni particles supported on cellulose fibers showed little agglomeration, even after a 168-h reforming reaction, but superior catalytic activity and long-term durability compared to a Ni/Al₂O₃ model catalyst. One of the reasons for these results was the lower extent of coking originating from the carbonaceous support. Another reason for these results was the high dispersion of Ni particles on the cellulose support, which was caused by the presence of alkaline earth metals such as Ca and Mg in the original structure of the support. Alkaline earth metals in the shape of nanosized particles significantly improved Ni dispersion and the interaction between the Ni particles and the support; they also retarded the agglomeration and sintering of the Ni particles. The cellulose fibers treated with different conditions were characterized by Raman and were observed by scanning and transmission electron microscopy. X-ray diffraction was performed to estimate Ni particle size before and after the catalytic usage. The interaction between the Ni particles and the support was measured by X-ray photoelectron spectroscopy.

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1. Introduction

Many studies have been conducted concerning the use of carbon as a catalytic support [1–5] due to its many desirable properties, including its low-cost, high surface area, the possibility to modify its pore size distribution and surface functionalities, and the ability for facile recovery of active metals from spent catalysts through the burn-off of supports. Among the various types of carbons, porous carbons are suitable as catalytic supports because they have a much higher surface area than conventional carbon black, and their pores are often used as catalytic reactors.

Two main techniques for the synthesis of porous carbon currently exist: (i) the use of silica or zeolite as a template for carbonization which leads to the production of porous carbon [6–10], and (ii) the use of block copolymers as structure-directing agents for the synthesis of ordered porous carbons [11]. However, these processes for producing porous material are not easy and require special materials for controlling pore size and shape. Most porous carbon is obtained from coal, pitch, or petroleum, and carbon from these sources exhibits a small surface area and a wide distribution of pore sizes. Recently, the simple production of porous carbons based on biomass resources has been achieved in several

studies [12,13]. However, most of these studies are objected to the synthesis of porous carbons, and only a few of them used the resultant carbons as a catalytic support [13].

The aim of this study is to synthesize a porous carbon support from natural cellulose fibers and to investigate the catalytic performance of a cellulose-supported Ni catalyst in a CO₂ reforming of CH₄, which is an attractive reaction for the conversion of two main green house gases into the valuable (CO + H₂) mixture of great value. When carbonaceous support is used as a support of reforming catalyst, the main drawback of conventional dry reforming process, the coke formation due to the lower H/C ratio of this reaction [14,15], can be solved. That is, it is known that a metal catalyst supported on carbon has a higher coke resistance than conventional Al₂O₃ [16,17]. For instance, a NiMo catalyst supported on activated carbon displayed a higher tolerance to coke deposition compared to an Al₂O₃-supported catalyst during ethylene conversion.

Among the numerous fibrous resources available that have large amount of pores and surface areas such as bamboo, yucca, cotton, jute, and coconut [18–21], henequen was selected as our source of porous carbon support; it is inexpensive and has an attractive morphology as a catalytic support, having a honeycomb-like channel structure. Henequen is a major plantation fiber indigenous mostly to the tropical regions of Africa (central and south Africa) and Asia (particularly china), similar to sisal [22]. Notably, most of natural cellulose fibers, including henequen, contain a significant amount of alkaline earth metals such as Ca and Mg in their own structures

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[23]; these earth metals are hypothesized to increase the activity and long-term durability of the reforming catalyst. Hou et al. [24] used Ca-promoted Ni/ α -Al₂O₃ for their CH₄ reforming of CO₂, and they found that Ca improved Ni dispersion, strengthened the interaction between Ni and Al₂O₃, and retarded sintering. Vizcaino et al. [25] incorporated Ca and Mg into CuNi/SBA-15 in an ethanol steam reforming, and they found an increase in the dispersion of the Cu–Ni phase, an enhancement in catalytic activity, higher hydrogen selectivity, and lower coke deposition of the catalyst. Carrero et al. [26] found that the Cu–Ni/SiO₂ catalyst containing Ca and Mg shows the reduction in Cu–Ni particle size, increase in the metal–support interaction, and higher resistance to coke deposition. Natural cellulose fibers, especially henequen, already contain appreciable amounts of Ca and Mg as highly dispersed, nano-sized particles, making them exceedingly effective in reforming reactions.

We developed techniques for the synthesis of a porous carbon support from henequen, and Ni particles were deposited onto the carbonized support. The resultant Ni/cellulose catalysts were applied to CO₂ reforming of CH₄, and the catalytic activities and long-term durabilities of the catalysts were compared with those of the Ni/Al₂O₃ model catalyst. The surface of cellulose fibers was investigated by scanning electron microscopy (SEM) before and after carbonization, and the Brunauer–Emmett–Teller (BET) surface areas were obtained for each sample. Further surface characterizations including Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were also performed.

2. Experiments

2.1. Pretreatment of cellulose fibers

Cellulose fibers were first treated with electron beam irradiation using an electron accelerator (ELV-4 type, EB-tech) for the removal of impurities such as wax and pectin substances [27]. The resultant fibers were cut into small fragments (0.1–1-mm wide by 1–2-mm long) in liquid nitrogen, and then the samples underwent carbonization to remove any hydrocarbon impurities. Carbonization was performed in a quartz tube reactor installed in a furnace heated to 500 °C, 700 °C, 900 °C, 1100 °C or 1300 °C and maintained for 2 h in an H₂/N₂ atmosphere (H₂:N₂ = 1:4, v/v). Next, the carbonized fibers underwent chemical pretreatment for surface oxidation, where the samples were immersed in a 1:1 (v/v) mixed solution of H₂SO₄ (98%) and HNO₃ (60%) for 15–360 min. The resultant fiber samples were washed with deionized water several times and dried at 110 °C in an oven for 12 h.

2.2. Catalyst synthesis

For the carbonized-cellulose fibers to be prepared as catalytic supports, Ni/cellulose(X) catalysts were made by a conventional wet-impregnation method, where X in Ni/cellulose(X) denotes the carbonization temperature. A 0.5-M aqueous Ni solution was prepared using Ni(NO₃)₂·6H₂O (98.5%, Aldrich) as a precursor, and the pretreated fiber samples were incubated in this Ni solution, while undergoing ultrasonic treatment for 1 h. After that time, the fiber samples were further immersed in the Ni solution for another 12 h and then filtered and dried in a 110 °C oven for 24 h. The resultant catalyst samples were calcined at 450 °C for 4 h in a N₂ atmosphere. The model catalyst, Ni/Al₂O₃ (20 wt% Ni), was prepared by incipient wetness impregnation method using γ -Al₂O₃ (Strem, 97%, 150 m² g^{−1} surface area and 0.7 cm³ g^{−1} pore volume) as a support and aqueous solution of Ni(NO₃)₂·6H₂O as a Ni precursor. The resultant catalysts were dried in air at 110 °C for 12 h and then calcined in air at 450 °C for 4 h.

2.3. Catalytic activity

The catalytic activity of the Ni/cellulose catalyst was estimated for the CO₂ reforming of CH₄, which was performed in a quartz tube reactor (20-mm i.d.) using a fixed-bed mode. Before each reaction, each catalyst was treated with flowing 5% H₂ diluted with Ar at 450 °C for 2 h in order to reduce NiO to elemental Ni, and then N₂ was purged through the latter for 1 h to remove impurities. A CO₂ reforming of CH₄ was performed at 700 °C with a vol. ratio of CO₂ to CH₄ equal to 1 and the space velocity was 120,000 ml/h g_{cat}. The conversion of CH₄ was measured by a gas chromatograph (GC, HP7890) connected to the outlet of the quartz tube reactor.

2.4. Surface characterizations

The surface of each fiber sample carbonized at a different temperature was observed using scanning electron microscopy (SEM, HITACHI S-4700), and Raman spectroscopy (HR800, Horiba jobin yvon) was used to follow the structural changes of the samples upon increase of the carbonization temperature. The BET surface area, average pore volume and average pore diameter of each sample was measured using an ASAP2010 (Micromeritics).

After pretreatment for surface oxidation, X-ray photoelectron spectroscopy (XPS, Thermo Multilab2000) was used for the detection of surface functional groups and estimation of the extent of surface oxidation. Ni particles deposited on the cellulose fiber support were investigated by transmission electron microscopy (TEM,

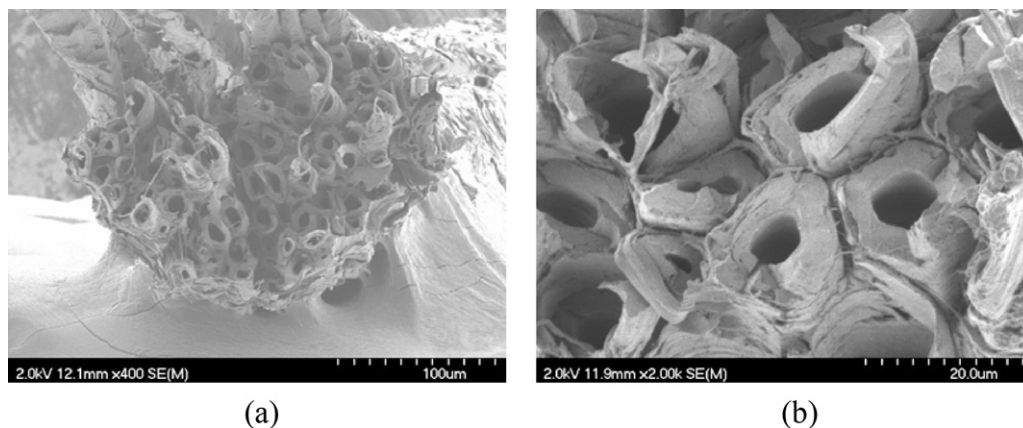


Fig. 1. SEM images of pristine cellulose fiber samples treated with an electron beam (100 kGy), shown in different scales of magnification.

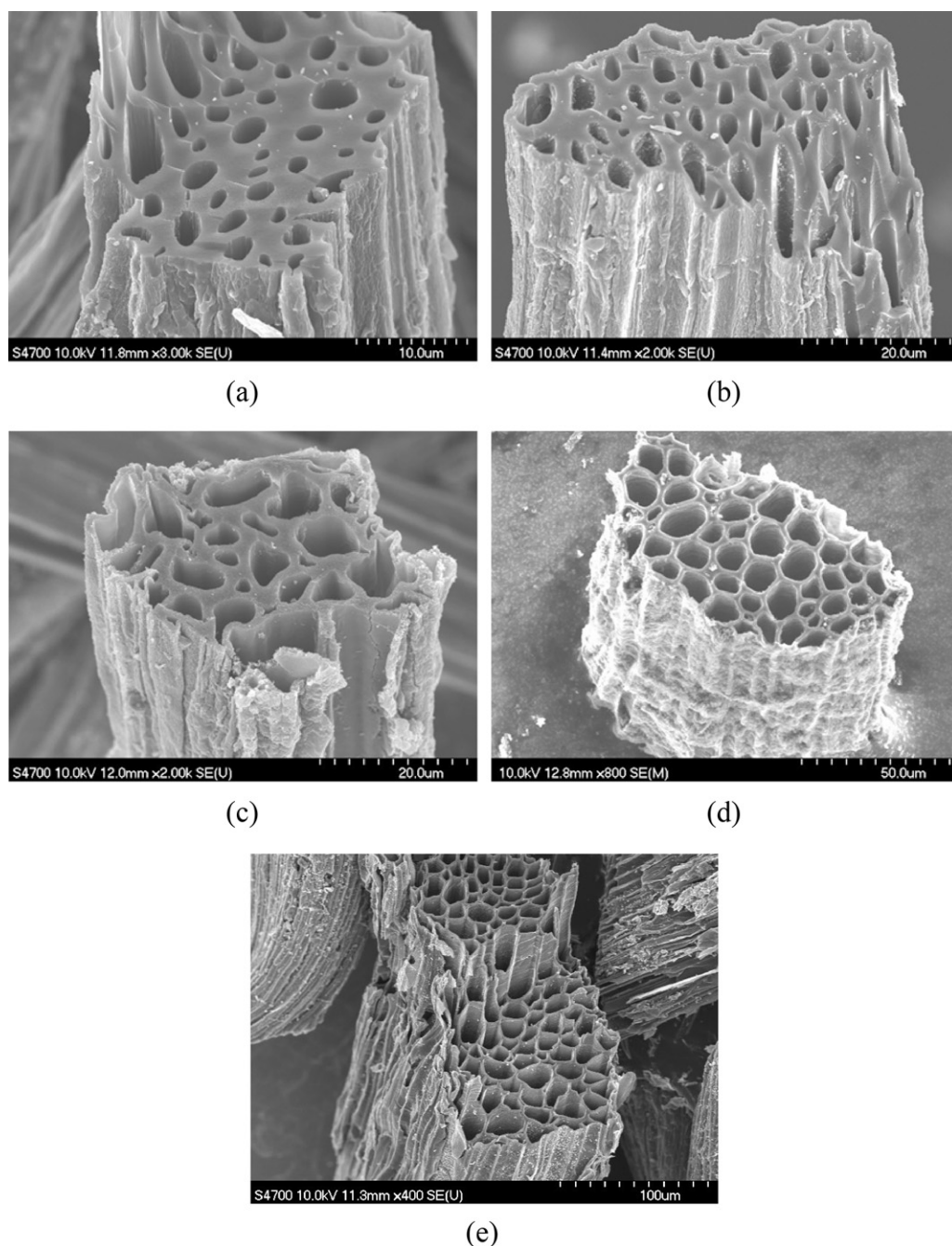


Fig. 2. SEM images of cellulose fiber samples carbonized at different temperatures^a; (a) 500 °C, (b) 700 °C, (c) 900 °C, (d) 1100 °C and (e) 1300 °C.

^a Carbonization was performed in an H₂/N₂ atmosphere for 2 h (H₂:N₂ = 1:4, v/v, temperature was raised from 25 °C to the target temperature at a ramping rate of 10 °C/min).

FEI/Tecna F30 Super-Twin) and the chemical composition of each sample's surface was determined by an energy-dispersive X-ray analysis (EDAX, DEAX/Genesis) instrument equipped with a Link ISI analyzer and a Pentafet detector (Oxford).

The Ni content in each catalyst was measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin-Elmer). The carbon content of the catalyst before and after usage in the catalytic reaction was measured by elemental analysis (EA, Leco/TriSpec CHN-1000). X-ray diffractions (XRD, Rigaku DMAX-2500) of each catalyst were also obtained to estimate the crystalline phase and the Ni particle size before and after the catalytic reactions.

The metal surface area and metal dispersion were estimated by H₂ pulse-chemisorption technique using Autochem

2910 (Micromeritics). Catalysts (50 mg) were placed into a quartz U-type reactor and reduced at 450 °C for 2 h in 20% H₂–He flow then flushed with He flow at ambient temperature for 1 h. H₂ adsorption was conducted 5% H₂–He flow at 50 °C. XPS was used to estimate the surface compositions and the interaction between the catalyst metal and support.

H₂-temperature programmed reduction (TPR) was carried out in ascending-temperature- and isothermal conditions. Before the TPR run, each catalyst was treated in Ar gas at 300 °C for 2 h, and the hydrogen consumption was monitored using thermal conductivity detector (TCD) of Autochem 2910 (Micromeritics). In H₂-TPR in ascending temperature condition, the temperature was ramped from room temperature to 1000 °C with a ramp of 10 °C/min. H₂-TPR spectra in isothermal condition was obtained at 450 °C for 3 h.

Table 1

BET surface areas, pore volumes and average pore diameters of the cellulose fibers treated at different temperatures.

Temperature (°C)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Ave. pore diameter (Å)
Pristine ^a	6	–	–
500	233	0.04	16
700	421	0.18	17
900	589	0.33	22
1100	990	0.66	27
1300	58	0.03	102
1500	36	0.02	118

^a Cellulose fiber samples treated with an electron beam (100 kGy).

In both cases, 10% H₂/Ar mixture gas was used at a flow rate of 30 ml/min.

3. Results and discussions

3.1. Surface characterizations

3.1.1. Cellulose fibers treated with an electron beam

Cellulose fibers were first treated with an electron beam (100 kGy) and which were observed using SEM as shown in Fig. 1. This figure indicates that pristine cellulose fibers, particularly henequen, have many 5–10-μm-wide microchannels and the inner and outer surfaces of these fibers consist of lots of pores. These properties suggest their potential as a catalytic support or as a honeycomb-like reactor for catalysis.

3.1.2. Thermal treatment of cellulose fibers

The electron beam-treated fiber samples were chopped into short fractions of 1–2 mm in length. The fibers were then carbonized at various temperatures (500 °C, 700 °C, 900 °C, 1100 °C, 1300 °C, and 1500 °C) for 2 h under a H₂ flow diluted with N₂ (H₂:N₂ = 1:4, v/v). The SEM images of the carbonized samples are shown in Fig. 2. It is notable that the thickness of the channel wall was significantly decreased with the increase in carbonization temperature. The reason for this observation may be that hydrocarbon impurities are burned off during the carbonization process, and this burn-off rate became more rapid in the samples treated at higher temperatures.

Table 1 indicates that the BET surface area increased in parallel with the carbonization temperatures from 500 °C to 1100 °C for each sample. However, the surface area abruptly decreased at temperatures higher than 1100 °C, which is possibly due to the widening and collapse of micropores into meso- or macropores and the shrinkage of cellulose structures. Overall, these results indicate that henequen fiber samples carbonized at temperatures higher than 1100 °C are not useful as catalytic supports.

Raman spectra of the cellulose fiber samples carbonized at different temperatures are shown in Fig. 3. In this figure, two large peaks were observed: one at 1344 cm⁻¹ (corresponding to the disordered, or D, band) and the other at 1581 cm⁻¹ (corresponding to the graphite, or G, band) [28]. The peak intensity ratio of the D band to G band (*I*_D/*I*_G) is often suggested to be an important indicator for determining the extent of graphitization; in short, as the *I*_D/*I*_G decreases, the graphitization degree increases [28,29]. However, in this study, the *I*_D/*I*_G value gradually increased with increasing temperature: 0.7 at 500 °C, 0.9 at 700 °C, 1.3 at 900 °C, 1.4 at 1100 °C, and 1.3 at 1300 °C, respectively. According to previous literature [30], all carbonaceous materials follow the same graphitization process, despite the degree of crumpling caused to their layers: single basic structural units (BSUs) are usually present below 600 °C, but then these units start to associate face-to-face into distorted columns at 900–1500 °C. Next, adjacent columns coalesce into distorted

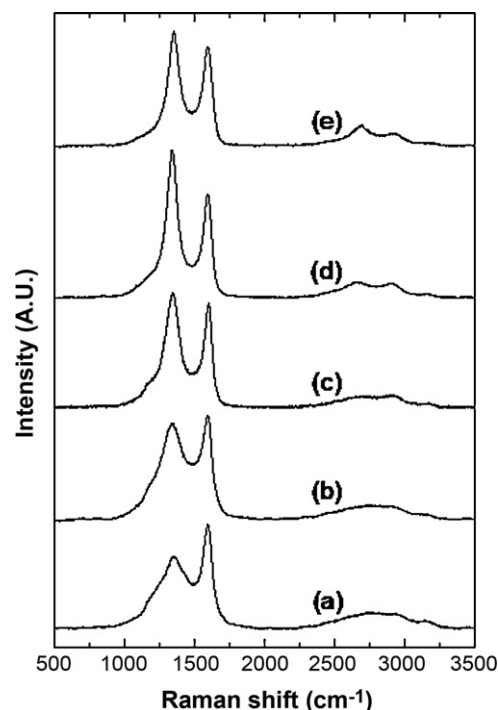


Fig. 3. Raman spectra of cellulose fiber samples carbonized at different temperatures^a: (a) 500 °C, (b) 700 °C, (c) 900 °C, (d) 1100 °C and (e) 1300 °C.

^a Carbonization was performed in an H₂/N₂ atmosphere for 2 h (H₂:N₂ = 1:4, v/v, temperature was raised from 25 °C to the target temperature at a ramping rate of 10 °C/min).

wrinkled layers at 1500–1900 °C, and then the distorted layers stiffen, becoming flat and perfect in the last stage at 2100–2600 °C. The cellulose fibers used in this study were treated at 500–1300 °C. At these low temperatures, disordered columns of small fringes were created, increasing the intensities of the D bands over the G bands in the Raman spectra.

After the carbonization process, lots of particles were observed on the cellulose support, regardless of the treatment temperature. Fig. 4 exhibits the SEM images of the cellulose fibers treated at 700 °C (Fig. 4(a)) and 1100 °C (Fig. 4(b)). Both of these figures show numerous particles that are highly dispersed on their cellulose support with 20–100-nm diameters, and the size and population of these particles do not vary with the carbonization temperature. Our SEM-EDAX results in Fig. 4 indicate that the particles are mostly composed of alkali earth metals such as Ca and Mg, though the surface compositions are not the same between each targeted-site, which should be quite useful for enhancing the reforming activity and long-term durability of the Ni catalyst considering previous literatures [24–26,31].

3.1.3. Pretreatment for surface oxidation

The surfaces of most carbonaceous supports are inert and hydrophobic in nature. Thus, it is difficult to deposit metal nanoparticles by wet impregnation in a highly dispersed manner on these supports. In this respect, surface oxidation is effective for creating defects and allowing the dispersion of metal particles on surfaces. In this study, we treated the carbonized fiber samples using a mixed acid solution of H₂SO₄ and HNO₃ for 15–360 min before performing metal deposition. Each sample was characterized by XPS for the evaluation of surface oxidation, where the XPS spectra of the C 1s, O 1s, Ca 2p, Mg 1s, S 2p and N 1s peaks were obtained. The extent of surface oxidation was estimated from the spectral area of the O 1s peak, and the amounts of the alkaline earth metals on the cellulose surface were measured from the peaks of Ca 2p and Mg 1s. In the

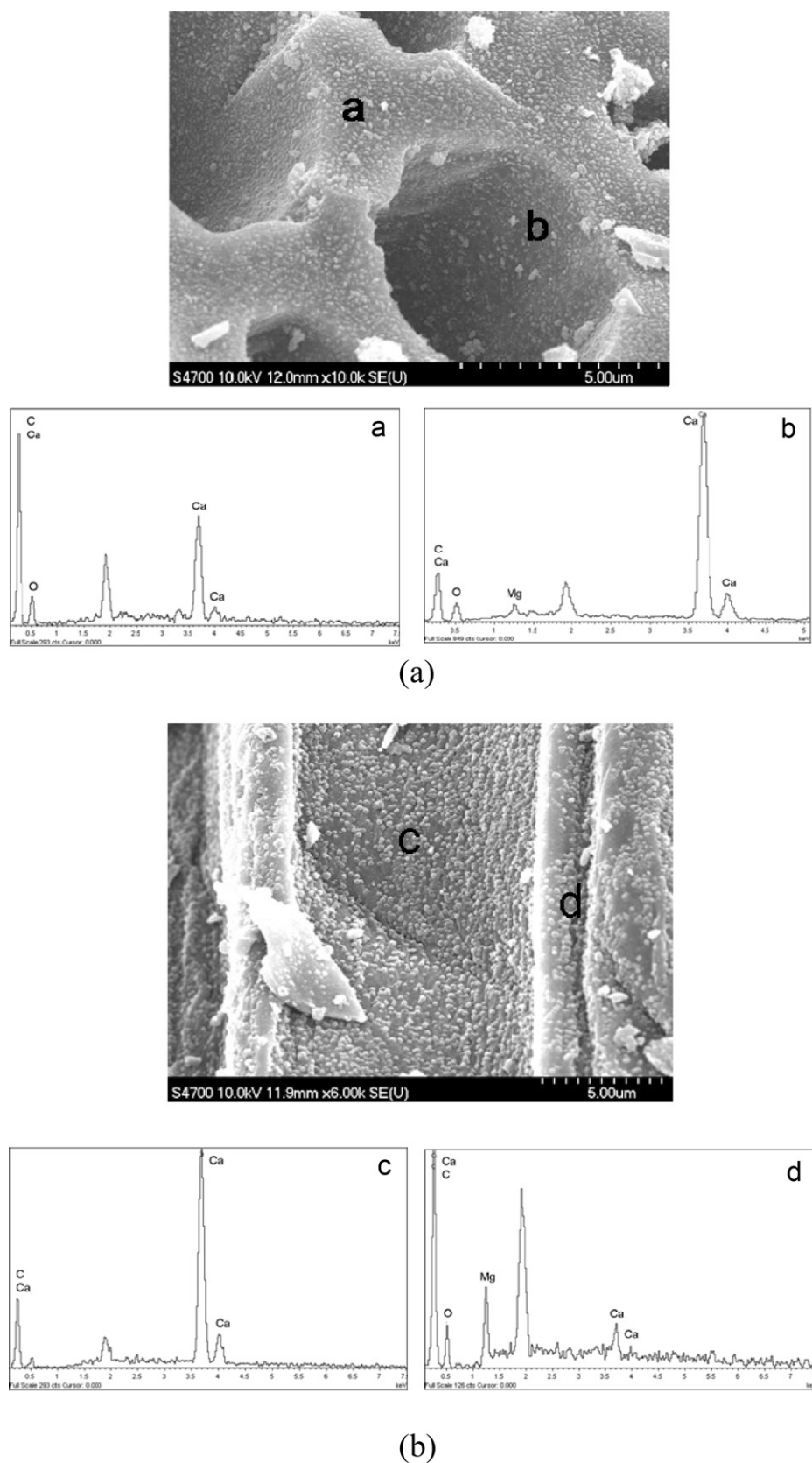


Fig. 4. SEM-EDAX images of cellulose fiber samples^a carbonized at (a) 700 °C and (b) 1100 °C.

^a Each sample was carbonized in H₂/N₂ atmosphere (H₂:N₂ = 1:4, v/v) for 2 h, then immersed in a mixed solution of sulfuric acid and nitric acid (H₂SO₄:HNO₃ = 1:1, v/v) for 3 h.

Table 2Atomic percentages of various elements on the cellulose fiber sample surfaces.^{a,b}

Samples	Time (min) ^c	C%	O%	Ca%	Mg%	S%	N%
Pristine	0	92.42	1.68	5.38	0.52	–	–
A	15	91.53	3.88	4.21	0.38	–	–
B	30	90.75	4.95	3.95	0.35	–	–
C	60	89.41	6.28	4.01	0.30	–	–
D	180	87.41	8.38	3.90	0.31	–	–
E	360	85.83	9.88	3.88	0.30	0.11	–

^a Atomic percentages were estimated from XPS data.^b Cellulose fiber samples were carbonized at 1100 °C for 2 h in H₂/N₂ atmosphere (H₂:N₂ = 1:1, v/v) before acidic pretreatment.^c Each sample was treated by a mixed solution of sulfuric acid (98% H₂SO₄, 50 ml) and nitric acid (14 M HNO₃, 50 ml) at 60 °C.

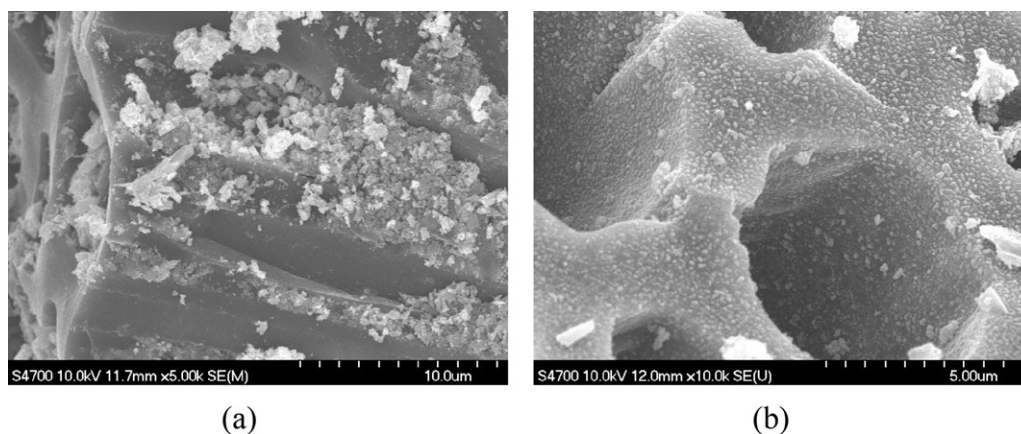
XPS spectra of C 1s and O 1s, no difference in the peak position was observed between untreated and treated samples. However, the O 1s peak area, as shown in Table 2, remarkably increased with longer treatment times, which was possibly due to the production of surface oxide groups, such as C–OH or C=O. Notably, the O 1s peak area increased rapidly over the initial 180-min treatment and then increased at a slower rate with further treatment. Based on these results, the cellulose fibers treated for 3 h in the acidic solution were adopted as the model support and used for our catalyst preparation. For Ca 2p and Mg 1s, each peak slightly decreased during the treatment time, which is probably due to the partial dissolution of surface metals in the acidic solution. Consequently, this slight dissolution of surface alkaline metals by acidic treatment was considered ineffective on the surface composition of the cellulose-supported catalysts. In all cases, the peaks caused by the acidic treatment for S 2p and N 1s were negligible, which suggested that the acid solution was almost completely removed from the samples via the washing process.

Fig. 5 shows the SEM images of the Ni particles supported on carbonized cellulose fibers (Fig. 5(a)) and those on the fibers which underwent the acidic treatment after the carbonization (Fig. 5(b)). Fig. 5(a) shows that most of the Ni particles are agglomerated on the outer surface and are stuck to the inner channel of the cellulose fibers. However, Fig. 5(b) indicates that the Ni particles are well-dispersed on the outer surface and inside the channels. The diameters of the Ni particles in Fig. 5(b) are 2–10 nm in size, which are much smaller than those of the untreated fibers (Fig. 5(a)). These results indicate that the surfaces of the cellulose fibers became more hydrophilic because of the surface defects created by oxidation: thus, the Ni particles could be selectively deposited on the defects of the support in a highly dispersed manner.

From the above results, we used the cellulose fibers treated at temperatures between 700 °C and 1100 °C as a support of Ni catalyst, because the supports treated below 700 °C or above 1100 °C has relatively small surface area. Therefore, our henequen fibers were treated at 700 °C, 900 °C, and 1100 °C for 2 h with a H₂ flow mixed with N₂, and then they were treated in an acidic solution for surface oxidation. The resultant cellulose fibers were used as the support for the Ni catalyst, which were then tested for their performance in the CO₂ reforming of CH₄.

3.2. Catalytic performance of Ni/cellulose catalyst

The catalytic performance of Ni particles supported on carbonized cellulose fibers was measured for a CO₂ reforming of CH₄ and the result was compared with that obtained by using a Ni/Al₂O₃ model catalyst. Fig. 6 shows CH₄ conversions, CO₂ conversions and H₂ yields obtained by using various catalysts. When Ni/cellulose(700) is used as a catalyst (Fig. 6(a)), the reforming reaction proceeds very slowly during the reaction time. However, in the case of Ni/cellulose(900) (Fig. 6(b)), the initial CH₄ conversion increased up to 40%, but it abruptly decreased to about 10% within 5 h. These results indicate that the cellulose supports treated below 1100 °C are not stable in the reforming reaction. That is, cellulose(700) and cellulose(900) contain relatively large amounts of hydrocarbon impurities than cellulose(1100). Those impurities often experience catalytic gasification due to the presence of H₂ or steam during the reforming reaction, and removed as CH₄, CO₂ and CO gases over Ni catalysts [32]. The values for total pore volumes and average pore sizes, though the results are not shown in this manuscript, designate that cellulose(700) and cellulose(900) showed widening of pores and loss of surface area after the usage in

**Fig. 5.** SEM images of Ni catalysts^a supported on cellulose fiber samples^b (a) before acidic pretreatment and (b) after acidic pretreatment.^c^a Each catalyst was prepared by wet-impregnation and contains 20 wt% Ni.^b Carbonization was performed at 1100 °C in a H₂/N₂ atmosphere (H₂:N₂ = 1:4, v/v) for 2 h.^c Cellulose fiber samples were immersed in a mixed solution of sulfuric acid and nitric acid (H₂SO₄:HNO₃ = 1:1, v/v) for 3 h.

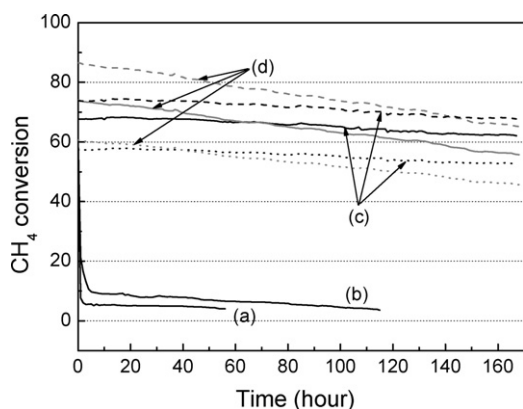


Fig. 6. CH₄ conversion (solid line), CO₂ conversion (dashed line), and H₂ yield (dotted line) in CO₂ reforming of CH₄ using (a) Ni/cellulose(700), (b) Ni/cellulose(900), (c) Ni/cellulose(1100), and (d) Ni/Al₂O₃. Ni loading of each catalyst is 20 wt%.

the reforming reaction. In other aspects, the carbonaceous support treated at temperatures lower than 1500 °C are mostly comprised of amorphous structures [30]. Nevertheless, the BSUs are associated more actively into distorted columns with the increase in carbonization temperature, as mentioned in Section 3.1.2, accordingly cellulose(1100) shows higher stability than cellulose(700) or cellulose(900) in the reforming reaction at high temperatures.

In the case of Ni/cellulose(1100) (Fig. 6(c)), the initial CH₄ conversion was about 68%, and catalytic activity was only slightly decreased by 6% after 168 h of reaction time. When Ni/Al₂O₃ was used as the catalyst, the initial CH₄ conversion was 73%, which is higher than the value obtained by Ni/cellulose(1100). However, this higher activity of Ni/Al₂O₃ decreased more rapidly compared to that of Ni/cellulose(1100) as time passed, and the conversion of the former was lower than that of the latter after 70 h. Similar trends are shown in CO₂ conversions and H₂ yields, though the absolute values and the turning points are not the same in each case.

These results indicate that our cellulose fiber support carbonized at a temperature higher than 1100 °C had superior activity and stability in the reforming reaction. These results are likely caused by the resistance of the carbon support [16,17]. The presence of alkali earth metals also suggested to enhance the coke resistance of the reforming catalysts; Carrero et al. [26] have studied the effect of Ca and Mg addition to Cu-Ni/SiO₂ catalysts for ethanol steam reforming. In this study, they suggested that the added Ca and Mg in the reforming catalyst promote the formation of disordered carbon, which is known to be more reactive and easily removed during the reforming reaction. Consequently, the catalyst containing Ca and Mg shows the resistance against coke deposition.

We have measured the carbon content of the Ni/cellulose(1100) and Ni/Al₂O₃ catalysts before and after use in the reforming reaction. After each catalyst was used for 168 h of reaction time, the carbon content of the former increased by 2.1 wt%, whereas that of the latter increased by 21.8 wt%. These findings suggest that cellulose(1100) has higher coke resistance than the conventional Al₂O₃ support. The effect of alkali earth metals on the catalytic activity and stability of the Ni/cellulose catalyst will be precisely discussed in the following Section 3.3.

3.3. The effects of alkali earth metals on catalytic activity and stability

As shown in our XPS results in Table 2 and the ICP-OES data in Table 3, the cellulose fibers used in this study contain a considerable amount of Ca and Mg regardless of their oxidation time or carbonization temperature. In Table 3, the metal content appeared to be increased but the carbon content decreased upon an increase in

Table 3

ICP-OES data of the cellulose fiber samples carbonized at different temperatures.

Carbonization temperature ^a (°C)	Component (wt%)		
	C	Ca	Mg
500	98.50	1.50	–
700	97.69	2.25	0.06
900	97.20	2.67	0.13
1100	95.86	3.89	0.31
1300	94.19	5.34	0.47

^a Each sample was carbonized in H₂/N₂ flow (H₂:N₂ = 1:4, v/v) for 2 h, then it was treated by a mixed solution of sulfuric acid (98% H₂SO₄, 50 ml) and nitric acid (14 M HNO₃, 50 ml) at 60 °C for 3 h.

carbonization temperature. The reason is because the hydrocarbon impurities are removed more effectively with the increase in carbonization temperature, but the metal contents are not affected by the treatment. After the cellulose fiber sample is treated at 1100 °C for 2 h, the sample contained 3.89% of Ca and 0.31% of Mg, which was quite similar to the metal contents of the sample measured by XPS (Table 2). The small differences between the metal contents measured by XPS (Table 2) and those obtained by ICP-OES (Table 3) are supposed to be caused by carbonization process. That is, the amorphous carbon in cellulose fiber structure is prone to be removed or shrunk by the carbonization at high temperatures, which is more serious in the outer surface than in the center of the stem. However, the metal components such as Ca and Mg are not affected by the carbonization treatment. Consequently, the metal contents in the outer surface, which was measured by XPS (generally within 10 nm depth), can be a little higher than the overall contents measured by ICP-OES.

Fig. 7 shows the TEM images and EDAX patterns of the cellulose fibers treated at 1100 °C (Fig. 7(a)) and of the same fibers with Ni particle deposits (Fig. 7(b)). The TEM image in Fig. 7(a) shows that the Ca and Mg particles with diameters of 2–10-nm-range are highly dispersed on the cellulose fibers; however, the peak for Mg did not appear in our EDAX results, possibly due to its small presence. Fig. 7(b) indicates that the Ni particles are highly dispersed between the Ca and Mg particles over the entire cellulose support, which is the main reason for the high catalytic activity of the Ni/cellulose catalyst. In short, the Ca and Mg particles act as obstacles between the Ni particles, resulting in barely agglomerated Ni during the catalytic reaction at high temperatures.

XRD patterns of various Ni catalysts were obtained for the analysis of Ni crystalline phase and the estimation of average particle size before and after catalytic usage. Fig. 8(a) shows that both NiO and NiAl₂O₄ are present on Al₂O₃ surface. The size of the NiO particles was calculated by the Scherrer equation to be 9 nm. In the case of Ni/cellulose(1100) (Fig. 8(c)), only the peaks for NiO were observed and the size of the particles was 7 nm, which is smaller than the former catalyst. After Ni/Al₂O₃ catalyst was used for a 168-h reforming reaction (Fig. 8(b)), a large peak for coke deposits was observed at 26 °C and most of NiO particles were transformed into NiAl₂O₄ spinel species and the average diameter of them was 21 nm. However, the particle size of the Ni particles on cellulose(1100) was around 10 nm (Fig. 8(d)). These results indicate that Ni particles supported on a cellulose support hardly agglomerated into bulky particles, even after long-term usage at high temperatures, because the alkaline earth metals, such as Ca and Mg, sterically hindered the agglomeration of the Ni particles.

We also performed H₂-chemisorption for the estimation of the dispersion and the particle size of Ni particles, and the results are summarized in Table 4. Ni dispersion of pristine catalyst is slightly higher in the case of Ni/cellulose(1100) than the case of Ni/Al₂O₃. When the catalysts are applied for the reforming reaction, Ni dispersion is decreased, which is more significant in the case of the

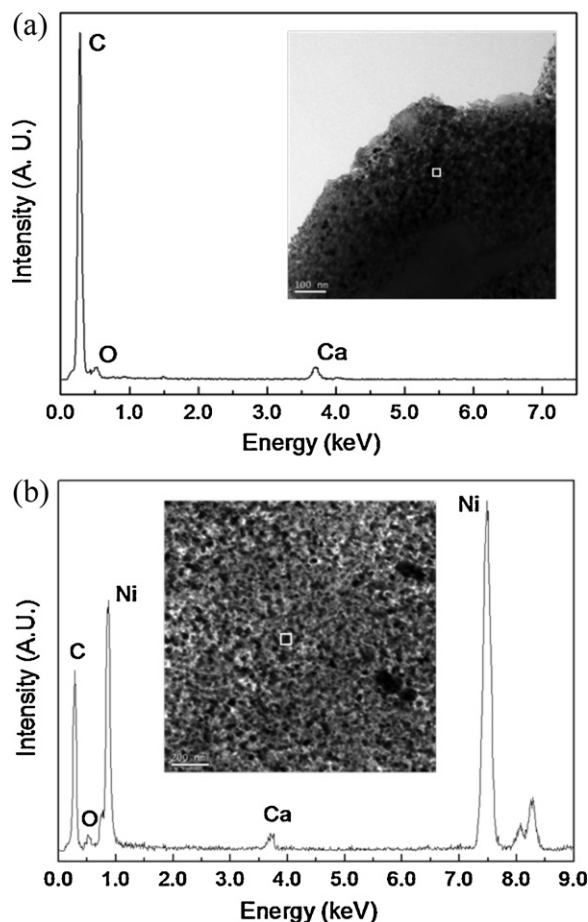


Fig. 7. TEM images and EDAX patterns of (a) cellulose(1100) fibers and (b) Ni/cellulose(1100).^a

^a Carbonization proceeded at 1100 °C in a H₂/N₂ atmosphere (H₂:N₂ = 1:4, v/v) for 2 h, and the Ni loading was 20 wt%.

latter. The reason is because Ni particles supported on Al₂O₃ are easily agglomerated during the reforming reaction, whereas those supported on cellulose(1100) are hardly agglomerated due to the presence of alkaline earth metals. The Ni particle sizes estimated from the H₂-chemisorption results are similar to those obtained by XRD patterns, which indicate that sintering of metal particles is more serious in the case of Ni/Al₂O₃ than Ni/cellulose(1100). Moreover, the coke deposition also reduces the amounts of H₂ uptake, which is more serious in the case of Al₂O₃-supported catalysts than cellulose-supported ones.

Table 4
Physicochemical characteristics of Ni/cellulose(1100) and Ni/Al₂O₃.

Catalyst	Ni/cellulose(1100)		Ni/Al ₂ O ₃	
	Before ^a	After ^b	Before ^a	After ^b
BET surface area (m ² g ⁻¹)	520.0	496.0	123.0	96.0
Ni surface area (m ² /g Ni) ^d	96.9	70.9	62.6	31.9
Ni dispersion (%)	14.6	10.7	9.4	4.8
Particle diameter (nm)				
By H ₂ -chemisorption	6.9	9.5	10.7	21.1
By XRD	7.0	10.0	9.0	21.0

^a BET surface before used in reforming reaction.

^b BET surface after used in 168-h reforming reaction.

^c H₂ uptake by supporting materials were took out from total H₂ uptake.

^d Ni surface area and Ni dispersion were calculated by assuming that atomic ratio of H/Ni equals to 1 and that cross-sectional area of atomic Ni is 6.49 × 10⁻²⁰ m²/Ni atom.

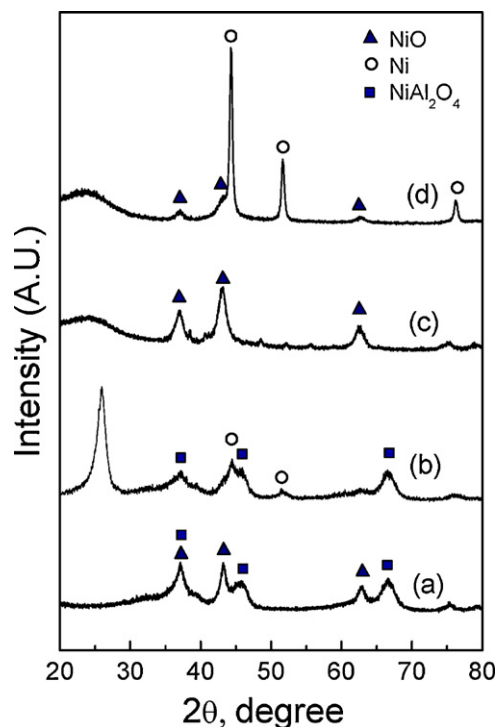


Fig. 8. Powder XRD patterns of (a) Ni/Al₂O₃ (raw), (b) Ni/Al₂O₃ (after used in a 168-h reforming reaction), (c) Ni/cellulose(1100) (raw), and (d) Ni/cellulose(1100) (after used in a 168-h reforming reaction).

The presence of alkaline earth metals are known to give rise to a strong metal-support interaction (SMSI) between the Ni particles and the cellulose support, and they retard the sintering of Ni particles [24,25,33]. In order to verify the SMSI between Ni particles and cellulose support created by the alkali earth metals present in the natural cellulose fibers, we obtained XPS spectra to examine the chemical composition of each catalyst, to estimate the metallic state of the Ni particles, and to measure the interaction between the cellulose supports and Ni particles. Fig. 9(a) shows the survey spectrum of Ni/cellulose(1100), which shows the Ni 2p, O 1s, Ca 2p and C 1s peaks. When the catalyst was used for a 168-h reforming reaction, no changes in the Ca 2p, O 1s and C 1s peaks were observed. This result shows that the interaction between the Ni and Ca metal particles does not change during the reforming reaction. However, the peak for Ni 2p_{3/2} does change after use in the 168-h reforming reaction.

Fig. 9(b) shows the XPS spectra of Ni 2p_{3/2} for several catalysts in this study. The Ni/Al₂O₃ model catalyst (Fig. 9(b)(i)) displayed a major peak at 855.4 eV (Peak I) and a satellite peak at 861.2 eV (Peak II), which corresponds to the Ni²⁺ state in NiO [34–36]. The Ni 2p_{3/2} spectra of Ni/cellulose(1100) (Fig. 9(b)(ii)) was slightly shifted to a higher energy level: a major peak was observed at 856.1 eV and the satellite peak was observed at 861.8 eV. These results may have been caused by the stronger interaction between the Ni particles and cellulose support. In short, the Ni particle size on the cellulose support was smaller than its size on Al₂O₃, such that the interaction between the Ni particles and support was also increased. The surface pretreatment of the cellulose support using our acidic solution also promoted the Ni-support interaction. Moreover, the presence of Ca and Mg not only improved the Ni dispersion but also enhanced the Ni-support interaction. When Ni/cellulose(1100) was used for the reforming reaction at 700 °C for 168 h (Fig. 9(b)(iii)), the Ni 2p_{3/2} spectral peaks appeared at similar positions to those of the pristine catalyst, which indicates that the metallic state of Ni was almost unchanged during the reaction. However, its major peak was split

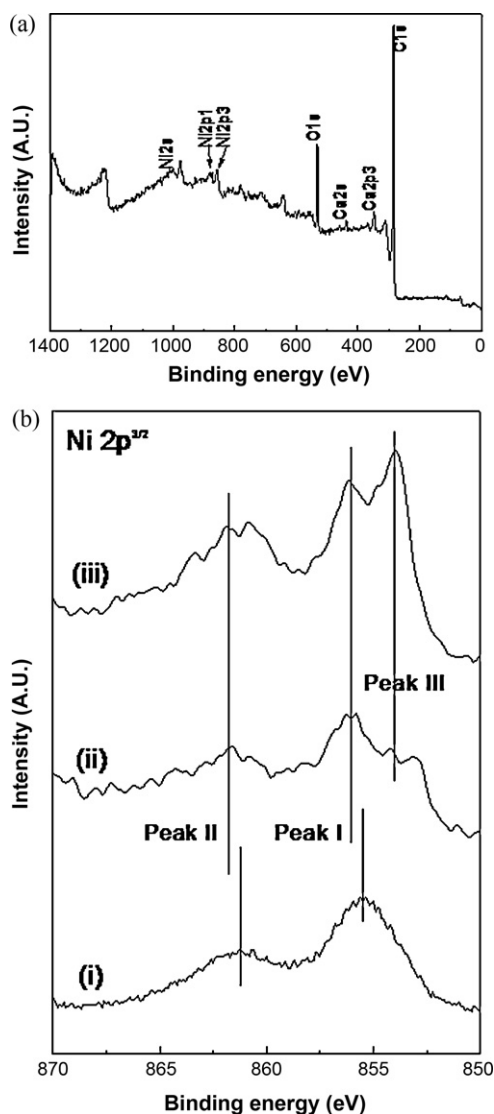


Fig. 9. XPS spectra of various catalysts; (a) Ni/cellulose(1100) (survey spectrum), and (b) Ni 2p_{3/2} for (i) Ni/Al₂O₃, (ii) Ni/cellulose(1100)^a (raw) and (iii) Ni/cellulose(1100)^a (after used in a 168-h reforming reaction).

^a Cellulose fibers were carbonized at 1100 °C for 2 h in a H₂/N₂ atmosphere (H₂:N₂ = 1:4, v/v), and then treated in a mixed acid solution (H₂SO₄:HNO₃ = 1:1, v/v) for 3 h. Ni loading of each catalyst was 20 wt%.

into a larger peak at 856.1 eV (Peak I) and a smaller shoulder at 854.0 eV (Peak III). The latter one was assigned to be elemental Ni⁰ [24,25,33,37–39] and was created by the reduction of NiO before the reforming reaction. These results are in good agreement with our XRD data (Fig. 8), which verify the presence of elemental Ni after use in a 168-h reforming reaction. Consequently, the Ni catalyst supported on a cellulose fiber shows high catalytic activity and long-term stability, which is caused mainly by the presence of alkali earth metals in the natural cellulose fibers.

For the investigation of metallic phase and the estimation of metal-support interaction, H₂-TPR was performed at ascending-temperature condition (Fig. 10(a)) and isothermal condition (Fig. 10(b)) for Ni/Al₂O₃ and Ni/cellulose(1100) catalysts. Fig. 10(a) designates that the reduction of Ni particles on both catalytic supports proceeds even at room temperature and which is almost finished at around 600 °C. It is noteworthy that Ni particles supported on Al₂O₃ are reduced at lower temperatures than those on cellulose(1100). In fact, the peak maximum appeared at 183 °C for Ni/Al₂O₃ and 201 °C for Ni/cellulose(1100). H₂-TPR spectra

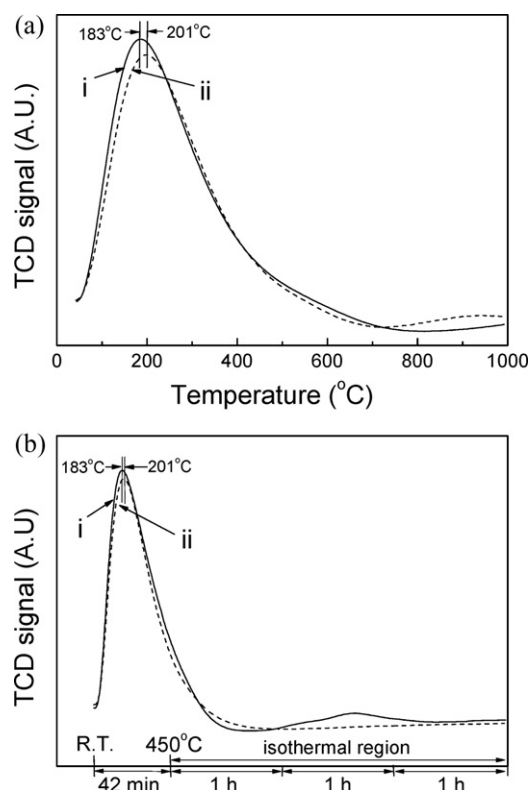


Fig. 10. H₂-TPR spectra of (i) Ni/Al₂O₃ and (ii) Ni/cellulose(1100) at different conditions; (a) ascending temperatures from room temperature to 1000 °C and (b) isothermal condition at 450 °C. In both cases, the ramping rate was 10 °C/min.

obtained at isothermal condition (Fig. 10(b)) indicate that Ni particles on both catalytic supports are fully reduced through our pre-reduction process as described in Section 2.4. The peak maximum of each spectrum appears at the same temperature as in Fig. 10(a). Both figures designate that the reduction of Ni particles is easier on Al₂O₃ than on cellulose(1100), which is supposed to be caused by stronger interaction between Ni–cellulose(1100) than Ni–Al₂O₃. In other words, the sizes of Ni particles are smaller and the metal-support interaction is stronger in the case of Ni/cellulose(1100) than Ni/Al₂O₃, which is possibly due to the presence of alkaline earth metals in cellulose fiber structure.

4. Conclusion

A new type of catalytic support was synthesized using natural cellulose fibers, specifically henequen fibers. This new cellulose support displays a high surface area and a large number of pores without specific activation treatment. In the CO₂ reforming of CH₄, Ni particles supported on cellulose fibers showed higher catalytic activity and long-term stability compared to those of a Ni/Al₂O₃ model catalyst, which is mainly due to the high dispersion and low extent of agglomeration of Ni nanoparticles in the catalyst. Notably, cellulose fibers naturally contain alkaline earth metals, such as Ca and Mg, in their structure, which can enhance Ni–cellulose interactions, improve Ni dispersion, and retard the sintering of Ni particles. Our XRD patterns and H₂-chemisorption data show that the agglomeration of Ni particles during the reforming reaction is more serious in the case of Ni/Al₂O₃ than Ni/cellulose(1100). The interaction between the Ni particles and support, which improves the Ni dispersion and long-term durability of the catalyst, is larger in the case of Ni/cellulose(1100) than Ni/Al₂O₃, as measured by XPS. Consequently, cellulose-supported metal catalysts can solve two main drawbacks of conventional Ni/Al₂O₃ catalyst in the reforming

reaction, metal sintering and coke deposition, and this successful derivation of a porous carbon support from natural cellulose fibers opens a new avenue for the catalytic application of various biomass resources that have been disposed without creating added cost.

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